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(71) Applicant: CLOPAY PLASTIC PRODUCTS COMPANY, INC. [US/US]; Suite 1600, 312 Walnut Street, Cincinnati, OH 45202 (US).

(72) Inventors: WU, Pai-Chuan; 11053 Huntwicke Place, Cincinnati, OH 45241 (US). RYLE, Thomas, R.; 5029 Idlewild Road, Burlington, KY 41005 (US).

(74) Agents: JOSEPHIC, David, J. et al.; Wood, Herron & Evans, L.L.P., 2700 Carew Tower, Cincinnati, OH 45202 (US).

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(54) Title: AIR AND MOISTURE VAPOR BREATHABLE BIODEGRADABLE FILMS AND METHOD OF MANUFACTURE

(57) Abstract: Biodegradable films permeable to moisture vapor and air which act as barriers to liquid are made by a high speed method. The films have high moisture vapor transmission rates (MVTRs) on the order of about 1000 to about 4500 g/m<sup>2</sup>/day according to ASTM E96E and air breathability of about 30 to about 2000 cc/cm<sup>2</sup>/min at 90 psi air pressure.

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**AIR AND MOISTURE VAPOR BREATHABLE BIODEGRADABLE  
FILMS AND METHOD OF MANUFACTURE****RELATED APPLICATIONS**

This application is a continuation-in-part application of Application Serial No. 09/480,374, filed January 10, 2000, which is, in turn, a continuation-in-part application of Application Serial  
5 No. 09/080,063, filed May 15, 1998, now U.S. Patent No. 6,013,151, and Application Serial No. 09/395,627, filed on September 14, 1999. All of the above applications are incorporated herein in their entireties by reference.

**FIELD OF THE INVENTION**

10           The present invention relates to air and moisture vapor breathable biodegradable plastic films and to processes for their manufacture.

**BACKGROUND OF THE INVENTION**

15           Methods of making plastic film date back many years. For example, more than thirty years ago U. S. Patent No. 3,484,835 (1968)

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issued to Trounstone, et al., and it is directed to embossed plastic film having desirable handling characteristics and fabricating useful articles such as diapers. Since that time, many patents have issued in the field. U. S. Patent No. 4,376,147 (1983) discloses an embossed cross  
5 direction (CD) and machine direction (MD) film. U. S. Patents Nos. 5,202,173 (1993) and 5,296,184 (1994) teach an ultra-soft thermoplastic film which was made by incrementally stretching the embossed film and the formation of perforations to achieve breathability. The film may include fillers. Polymer films of polycaprolactone (PCL) and  
10 starch polymer or polyvinyl alcohol (PVOH) upon incremental stretching also produce breathable products, as disclosed in U. S. Patents Nos. 5,200,247 and 5,407,979. More recently, U. S. Patent No. 5,865,926 issued for a method of making a cloth-like microporous laminate of a nonwoven fibrous web and thermoplastic film having air and  
15 moisture vapor permeabilities with liquid-barrier properties.

Methods of making microporous film products have also been known for some time. For example, U. S. Patent No. 3,832,267, to Liu, teaches the melt-embossing of a polyolefin film containing a dispersed amorphous polymer phase prior to stretching or orientation to  
20 improve gas and moisture vapor transmission of the film. According to the Liu '267 patent, a film of crystalline polypropylene having a dispersed amorphous polypropylene phase is first embossed prior to biaxially drawing (stretching) to produce an oriented imperforate film having

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greater permeability. The dispersed amorphous phase serves to provide microvoids to enhance the permeability of the otherwise impermeable film to improve moisture vapor transmission (MVT).

In 1976, Schwarz published a paper which described  
5 polymer blends and compositions to produce microporous substrates (Eckhard C.A. Schwartz (Biax-Fiberfilm), "New Fibrillated Film Structures, Manufacture and Uses", Pap. Synth. Conf. (TAPPI), 1976, pages 33-39). According to this paper, a film of two or more incompatible polymers, where one polymer forms a continuous phase and a second polymer  
10 forms a discontinuous phase, upon being stretched will phase separate thereby leading to voids in the polymer matrix and increasing the porosity of the film. The continuous film matrix of a crystallizable polymer may also be filled with inorganic filler such as clay, titanium dioxide, calcium carbonate, etc., to provide microporosity in the stretched polymeric  
15 substrate.

Many other patents and publications disclose the phenomenon of making microporous thermoplastic film products. For example, European patent 141592 discloses the use of a polyolefin, particularly ethylene vinyl acetate (EVA) containing a dispersed  
20 polystyrene phase which, when stretched, produces a voided film which improves the moisture vapor permeability of the film. This EP '592 patent also discloses the sequential steps of embossing the EVA film with thick and thin areas followed by stretching to first provide a film having

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voids which, when further stretched, produces a net-like product. U. S. Patents Nos. 4,452,845 and 4,596,738 also disclose stretched thermoplastic films where the dispersed phase may be a polyethylene filled with calcium carbonate to provide the microvoids upon stretching.

5 U. S. Patents Nos. 3,137,746; 4,777,073; 4,814,124; and 4,921,653 disclose the same processes described by the above-mentioned publications involving the steps of first embossing a polyolefin film containing a filler and then stretching that film to provide a microporous product. Other patent publications have issued, including WO 98/23673,

10 which are directed to thermoplastic copolyester films having improved moisture vapor transmission rates and are made by mixing a copolyester resin and an inorganic filler.

Biodegradable and/or compostable products help preserve environmental resources and prevent generation of additional waste.

15 Both manufacturers and consumers are aware of the finite amount of space in landfills and other disposal sites and may affirmatively seek biodegradable and/or compostable products over nonbiodegradable and/or noncompostable products. The need for biodegradability and/or compostability is particularly important in disposable, high use products

20 such as baby diapers, feminine hygiene products, hospital drapes, and the like.

Thermoplastic films that are biodegradable and/or compostable are known in the prior art. The above-mentioned U.S.

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Patent No. 5,407,979 discloses a biodegradable thermoplastic film composed of three components: an alkanoyl polymer, destructured starch, and an ethylene copolymer. The components can be extruded and the film can be stretched to form a breathable film. U.S. Patent  
5 No. 5,200,247 discloses a biodegradable thermoplastic film containing an alkanoyl polymer/polyvinyl alcohol (PVA) blend. U.S. Patent No. 5,196,247 discloses a compostable polymeric composite sheet and method of making or composting.

Totally biodegradable and/or compostable soft cloth-like  
10 composites are disclosed in U.S. Patent No. 5,851,937. The composites are made by incrementally stretching one or more plies of totally biodegradable and/or compostable nonwoven webs and plastic films to provide a soft cloth-like feel.

There still remain drawbacks to the production of breathable  
15 films and laminates which are liquid barriers. It is difficult to obtain a liquid barrier film of sufficient strength while maintaining the properties of biodegradability, air breathability and moisture vapor transmission.

#### **SUMMARY OF THE INVENTION**

This invention is directed to a biodegradable film which is  
20 both air and moisture vapor breathable, and is a barrier to liquid. These films have moisture vapor transmission rates (MVTRs) greater than about 1000 grams (gms) per m<sup>2</sup> per day and 100°F and 95% relative humidity

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(RH) according to ASTM E96E and air permeabilities greater than about 30 cc/cm<sup>2</sup>/min at 90 psi air pressure.

In the above-identified patent applications serial nos. 09/080,063 and 09/480,374, incrementally stretched films were disclosed having high MVTRs. These applications were directed to improvements in incrementally stretched embossed and unembossed films having MVTRs, preferably on the order of about 1200 to about 4500 gms/m<sup>2</sup>/per day. Breathable laminates of these films with nonwoven substrates were also disclosed.

10 This invention is directed to further improvements in biodegradable films and laminates which are both permeable to air and moisture vapor. In a broad form of the invention, the biodegradable film comprises a blend of a biodegradable thermoplastic polymer and a mechanical pore forming agent such as inorganic fillers of calcium carbonate, silica and zeolite. The pore forming agent in the film or  
15 laminate is activated upon stretching, preferably incremental stretching, to form a microporous film or laminate of a fibrous web and film. The biodegradable polymers such as polycaprolactone (PCL) blended with starch polymers or polyvinylalcohol (PVA) that may be film-formed are  
20 suitable. Other biodegradable polymers include polylactides (PLA), polyesters and copolyesters.

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The biodegradable films and laminates can be used for diaper  
backsheets, sanitary napkins and pads, and other medical, packaging and  
garment applications. The biodegradable film is especially suitable for  
these and other similar applications because of its air breathability,  
5 moisture vapor breathability and water impermeability. The benefits and  
properties of the biodegradable film of this invention and its method of  
manufacture will be further understood with reference to the following  
detailed description.

#### **DETAILED DESCRIPTION OF THE INVENTION**

10 It is the primary objective of this invention to produce an air  
and moisture vapor breathable biodegradable film having an air  
permeability of at least about 30 cc/cm<sup>2</sup>/min at 90 psi air pressure and a  
MVTR greater than about 1000 gms per m<sup>2</sup> per day and 100°F and 95%  
relative humidity (RH) according to ASTM E96E. It is the further  
15 objective of this invention to produce an incrementally stretched  
biodegradable thermoplastic film having these breathable properties of  
regular gauge, uniform porosity and without breakage.

##### **A. Biodegradable Film and Laminate Materials**

The biodegradable film composition can be achieved by  
20 formulating a biodegradable thermoplastic polymer with suitable additives  
and pore forming fillers to provide an extrudate or film. The film may be  
laminated with a nonwoven web. Calcium carbonate, barium sulfate,



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silica, and zeolite particles are the most common fillers. As developed above, it is known to provide biodegradable films with different polymer phases in the film so that when the film is stretched at ambient or room temperature, microvoids are produced to provide breathability and moisture vapor transmission. These methods are described in U.S. Patents Nos. 5,200,247, and 5,407,979. In contrast, this invention is directed to the use of inorganic fillers to provide high air permeabilities and high MVTRs with liquid barrier properties in biodegradable films.

As developed above, these and other objectives are achieved in a preferred form of the invention by first melt blending a composition of (a) about 40% to about 75% by weight of a biodegradable polymer of the type identified above, and (b) about 25% to about 60% by weight of an inorganic filler particles, for example, calcium carbonate, zeolite, silica, talc, barium sulfate, mica, and the like, then extruding said melt blended composition with other additives into a nip of rollers to form a film at a speed on the order of at least about 550 fpm to about 1200 fpm without draw resonance, and applying an incremental stretching force to said film at said speed along lines substantially and uniformly across the film and throughout its depth to provide a biodegradable microporous film.

More particularly, in preferred form, the melt blended composition consists essentially of about 60% to about 75% of a polyester such as aliphatic-aromatic copolyesters which are described in WO 98/23673 and that description is incorporated herein by reference.

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In particular, these thermoplastic copolyesters may comprise at least one aliphatic dicarboxylic acid, at least one aromatic dicarboxylic acid, and at least one aliphatic diol having from 4 to about 12 carbon atoms. Alternatively, the thermoplastic copolyester may comprise at least one aromatic dicarboxylic acid, at least one aliphatic diol and a polyalkylene ether. The aliphatic dicarboxylic acid is selected from the group consisting of adipic acid, glutaric acid, cyclohexanoic acid, and mixtures thereof; at least one of said aromatic dicarboxylic acids is selected from the group consisting of terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, and mixtures thereof; and at least one of said aliphatic diols is selected from the group consisting of 1,4-butanediol, cyclohexanedimethanol, a polyalkylene ether compound selected from the group consisting of poly(ethylene glycol), poly(tetramethylene glycol) and poly(propylene glycol), and mixtures thereof. The thermoplastic copolyester may comprise various combinations of aromatic dicarboxylic acid, aliphatic diols, cyclicaliphatic dicarboxylic acids, polyalkylene ethers, and the like, all described in the WO 98/23673 publication as examples of copolyesters within the scope of this invention.

Other polymers include ester-ether polyester (Hytrel and Armtel); nylon-ether polyester (Pebax); polyethylene terephthalate (PET); polyvinyl alcohol (PVA); polycaprolactone (PCL); starch; polylactide (PLA); a blend of starch and PVA, PCL, or PLA; polyesters such as

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polyhydroxy(butyrate) (PHB), polyhydroxy(valerate) (PHV); and mixtures thereof. Preferably, about 25-40% of calcium carbonate, silica, barium sulfate, or zeolite, having an average particle size of about 1 to about 10  $\mu$  is used.

5                   The biodegradable nonwovens may be laminated to the films and they include preferably melt-stable lactide polymers of the type disclosed in U.S. Patent No. 5,539,081, that is, polylactide nonwovens (PLA). All the filaments of the nonwoven are made entirely of a polymer or a mixture of polymers derived from lactic acid, that is L lactic acid,  
10   D lactic acid, or a mixture of L and D lactic acids. Other nonwovens which are biodegradable and/or compostable include cotton nonwovens, cellulosic nonwovens, aliphatic-aromatic copolyesters, and their blends.

                  In the above method, the melt-blended composition is slot-die extruded as a web through a cooling zone provided by an air knife,  
15   then into a nip of rollers to form a film at high speeds. Embossed or flat (non-embossed) films can be produced. Use of the air knife, as developed above, assists in the elimination of draw resonance, as is known, for example, by reference to U. S. Patent No. 4,626,574. In addition, as described in pending U. S. Application Serial No. 09/395,627, filed  
20   September 14, 1999, which is incorporated herein in its entirety by reference, devices for directing a stream of cooling gas to flow in the cooling zone substantially parallel to the web surface are used. For example, devices as shown in U. S. Patents Nos. 4,718,178 and

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4,779,355 may be used and the entire disclosures of these patents are also incorporated herein by reference. After cooling, an incremental stretching force is applied to the film or the laminate at high speeds along lines substantially uniformly across the film and throughout its depth to  
5 provide the incrementally stretched embossed or flat film having a high MVTR and air permeability.

The flat films are produced according to the principles of this invention upon extrusion of a web into a nip of rollers which provide a polished chrome surface to form a flat film. The flat film, upon  
10 incremental stretching, at high speeds, produces microporous film products having a high MVTR of greater than 1000 gms/m<sup>2</sup>/day. It has been found that flat film can be incrementally stretched more uniformly than embossed film. The stretching process may be conducted at ambient temperature, room temperature, or at an elevated temperature,  
15 as understood in the art. As also understood in the art, "ambient" means surrounding temperature or atmosphere which could be whatever process conditions exist surrounding the film. As described above, laminates of the microporous film may be obtained with nonwoven fibrous webs.

In a preferred form, the microporous laminate employs a film  
20 having a gauge or a thickness between about 0.25 and 10 mils and, depending upon use, the film thickness will vary and, most preferably, in disposable applications is the order of about 0.25 to 2 mils in thickness. The nonwoven fibrous webs of the laminated sheet normally have a

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weight of about 5 gms/yd<sup>2</sup> to 75 gms/yd<sup>2</sup>, preferably about 20 to about 40 gms/yd<sup>2</sup>. The composite or laminate can be incrementally stretched in the cross direction (CD) to form a CD stretched composite. Furthermore, CD stretching may be followed by stretching in the machine  
5 direction (MD) to form a composite which is stretched in both CD and MD directions. As indicated above, the microporous film or laminate may be used in many different applications such as baby diapers, baby training pants, catamenial pads and garments, and the like where moisture vapor and air transmission properties, as well as fluid barrier properties, are  
10 needed.

#### **B. Stretchers for the Microporous Film and Laminates**

A number of different stretchers and techniques may be employed to stretch the film or laminate of a nonwoven fibrous web and microporous-formable film. These laminates of nonwoven carded fibrous  
15 webs of staple fibers or nonwoven spun-bonded fibrous webs may be stretched with the stretchers and techniques described as follows:

##### **1. Diagonal Intermeshing Stretcher**

The diagonal intermeshing stretcher consists of a pair of left hand and right hand helical gear-like elements on parallel shafts. The  
20 shafts are disposed between two machine side plates, the lower shaft being located in fixed bearings and the upper shaft being located in bearings in vertically slidable members. The slidable members are

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adjustable in the vertical direction by wedge shaped elements operable by adjusting screws. Screwing the wedges out or in will move the vertically slidable member respectively down or up to further engage or disengage the gear-like teeth of the upper intermeshing roll with the lower intermeshing roll. Micrometers mounted to the side frames are operable to indicate the depth of engagement of the teeth of the intermeshing roll.

Air cylinders are employed to hold the slidable members in their lower engaged position firmly against the adjusting wedges to oppose the upward force exerted by the material being stretched. These cylinders may also be retracted to disengage the upper and lower intermeshing rolls from each other for purposes of threading material through the intermeshing equipment or in conjunction with a safety circuit which would open all the machine nip points when activated.

A drive means is typically utilized to drive the stationery intermeshing roll. If the upper intermeshing roll is to be disengageable for purposes of machine threading or safety, it is preferable to use an antibacklash gearing arrangement between the upper and lower intermeshing rolls to assure that upon reengagement the teeth of one intermeshing roll always fall between the teeth of the other intermeshing roll and potentially damaging physical contact between addenda of intermeshing teeth is avoided. If the intermeshing rolls are to remain in constant engagement, the upper intermeshing roll typically need not be

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driven. Drive may be accomplished by the driven intermeshing roll through the material being stretched.

The intermeshing rolls closely resemble fine pitch helical gears. In the preferred embodiment, the rolls have 5.935" diameter, 45° helix angle, a 0.100" normal pitch, 30 diametral pitch, 14½° pressure angle, and are basically a long addendum topped gear. This produces a narrow, deep tooth profile which allows up to about 0.090" of intermeshing engagement and about 0.005" clearance on the sides of the tooth for material thickness. The teeth are not designed to transmit rotational torque and do not contact metal-to-metal in normal intermeshing stretching operation.

## 2. Cross Direction Intermeshing Stretcher

The CD intermeshing stretching equipment is identical to the diagonal intermeshing stretcher with differences in the design of the intermeshing rolls and other minor areas noted below. Since the CD intermeshing elements are capable of large engagement depths, it is important that the equipment incorporate a means of causing the shafts of the two intermeshing rolls to remain parallel when the top shaft is raising or lowering. This is necessary to assure that the teeth of one intermeshing roll always fall between the teeth of the other intermeshing roll and potentially damaging physical contact between intermeshing teeth is avoided. This parallel motion is assured by a rack and gear

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arrangement wherein a stationary gear rack is attached to each side frame in juxtaposition to the vertically slidable members. A shaft traverses the side frames and operates in a bearing in each of the vertically slidable members. A gear resides on each end of this shaft and operates in  
5 engagement with the racks to produce the desired parallel motion.

The drive for the CD intermeshing stretcher must operate both upper and lower intermeshing rolls except in the case of intermeshing stretching of materials with a relatively high coefficient of friction. The drive need not be antibacklash, however, because a small  
10 amount of machine direction misalignment or drive slippage will cause no problem. The reason for this will become evident with a description of the CD intermeshing elements.

The CD intermeshing elements are machined from solid material but can best be described as an alternating stack of two different  
15 diameter disks. In the preferred embodiment, the intermeshing disks would be 6" in diameter, 0.031" thick, and have a full radius on their edge. The spacer disks separating the intermeshing disks would be 5 1/2" in diameter and 0.069" in thickness. Two rolls of this configuration would be able to be intermeshed up to 0.231" leaving 0.019" clearance  
20 for material on all sides. As with the diagonal intermeshing stretcher, this CD intermeshing element configuration would have a 0.100" pitch.



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### 3. Machine Direction Intermeshing Stretcher

The MD intermeshing stretching equipment is identical to the diagonal intermeshing stretch except for the design of the intermeshing rolls. The MD intermeshing rolls closely resemble fine pitch spur gears.

- 5 In the preferred embodiment, the rolls have a 5.933" diameter, 0.100" pitch, 30 Diametral pitch,  $14\frac{1}{2}^{\circ}$  pressure angle, and are basically a long addendum, topped gear. A second pass was taken on these rolls with the gear hob offset 0.010" to provide a narrowed tooth with more clearance. With about 0.090" of engagement, this configuration will
- 10 have about 0.010" clearance on the sides for material thickness.

### 4. Incremental Stretching Technique

- The above described diagonal, CD or MD intermeshing stretchers may be employed to produce the incrementally stretched film or laminate of nonwoven fibrous web and microporous-formable film to
- 15 form the microporous film products of this invention. For example, the stretching operation may be employed on an extrusion laminate of a nonwoven fibrous web of staple fibers or spun-bonded filaments and microporous-formable thermoplastic film. In one of the unique aspects of this invention a laminate of a nonwoven fibrous web of spun-bonded
- 20 filaments may be incrementally stretched to provide a very soft fibrous finish to the laminate that looks like cloth. The laminate of nonwoven fibrous web and microporous-formable film is incrementally stretched

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using, for instance, the CD and/or MD intermeshing stretcher with one pass through the stretcher with a depth of roller engagement at about 0.060 inch to 0.120 inch at speeds from about 550 fpm to 1200 fpm or faster. The results of such incremental or intermesh stretching produces  
5 laminates that have excellent breathability and liquid-barrier properties, yet provide superior bond strengths and soft cloth-like textures.

The following examples illustrate the method of making microporous film and laminates of this invention. In light of these examples and this further detailed description, it is apparent to a person  
10 of ordinary skill in the art that variations thereof may be made without departing from the scope of this invention.

#### **BRIEF DESCRIPTION OF THE FIGURES**

FIG. 1 is a microphotograph of the film surface of Example 1A at 1000X.

15 FIG. 2 is a microphotograph of a cross-section of Example 1A film at 2000X.

FIG. 3 is a microphotograph of the film surface of Example 1B at 1000X in the unstretched area due to intermeshing.

20 FIG. 4 is a microphotograph of the film surface of Example 1B at 1000X in the stretched area due to intermeshing stretching.

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FIG. 5 is a microphotograph of a cross-section of Example 1B film at 2000X through the stretched surface area.

### Examples 1A and 1B

A biodegradable copolyester of an aromatic-aliphatic type,  
5 as fully described in the examples of WO 98/23673, is employed in these examples. More specifically, a film having representative biodegradable copolyesters described in the examples of this publication, containing about 25% to about 40% zeolite or calcium carbonate, are extruded by using a conventional slot die cast film extrusion technique which is well  
10 known to a person of ordinary skill in the art. In particular, films having thicknesses of about 2 mil (50 grams per square meter) are extruded at melt temperatures on the order of about 425°F-475°F. A microphotograph of such a film surface is shown in FIG. 1, and a cross-section is shown in FIG. 2. The film was tested and found not to be air  
15 permeable, but had a MVTR (moisture vapor transmission rate) of 939 g/m<sup>2</sup>/day according to the ASTM E96E test method.

The film of Example 1A, when incrementally stretched at a temperature of about 72°F with CD engagement of 0.070 inch followed with MD engagement of 0.050 inch, with apparatus described above,  
20 became air breathable and had an increased moisture vapor transmission rate. The MVTR increased from 939 g/m<sup>2</sup>/day (Example 1A) to 2350 g/m<sup>2</sup>/day (Example 1B). The air permeability of the film having

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originally zero permeability (Example 1A), became 570 cc of air/cm<sup>2</sup>/min under 90 psi air pressure (Example 1B).

Microphotographs of the film surfaces and cross-sections of Examples 1A and 1B did show the embedded inorganic particles (see FIGS. 1-5). The high MVTR and air-permeable biodegradable film of this invention did have the pore formation around the inorganic particles upon incremental stretching (see FIGs. 4 and 5). Yet, the unstretched area did not show pore formation (see FIG 3). The cross-section of Example 1B film (see FIG. 5) clearly indicated that pores are connected to allow air flow. In Example 1A film (see FIG. 2, cross-section), there were no pore connections to allow air to flow through.

The mechanical properties of Example 1A film are as follows:

	Example A	Example B	Ratio of 1B/1A
Total Basis Weight (GSM)	50	35	0.7
Air flow cc/cm <sup>2</sup> /min at 90 psi	0	570	∞
MVTR (g/m <sup>2</sup> /day) ASTM E96E	939	2350	2.5
MD ultimate tensile (grams/inch)	1116	885	
CD ultimate tensile (grams/inch)	756	661	
MD elongation at break (%)	707	494	
CD elongation at break (%)	539	436	

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The biodegradable film of Example 1B is suitable for diaper backsheets, sanitary napkins, and health care garment applications where air flow (ventilation), high moisture vapor transmission, and liquid barrier properties are needed for skin care and comfort while wearing.

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**Examples 2A-2H**

In these Examples, copolyesters of the aromatic-aliphatic type as employed in Example 1A are extruded into a film in a similar fashion. These films of Examples 2A-2H are CD and/or MD stretched at room temperature to become air and moisture vapor breathable biodegradable films, as indicated below.

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Example	Intermeshing stretching (inches)		Air flow cc/cm <sup>2</sup> /min 90 psi air	Moisture Vapor Transmission Rate E96E gm <sup>2</sup> /day	Basis weight (GSM)	Stretch ration (before/after)
	CD	MD				
1A (reference)	0	0	0	939	50	0
2A	0.040	0	50	1365	48	1.05
2B	0.040	0.040	110	1665	45	1.11
2C	0.050	0	140	1665	45	1.11
2D	0.050	0.050	280	2122	39	1.28
2E	0.060	0	200	1895	40	1.25
2F	0.060	0.060	490	2350	33	1.51
2G	0.070	0	310	2122	36	1.39
2H	0.070	0.070	720	2652	29	1.72

Other biodegradable polymers such as the polylactides, polycaprolactones, starch, polyvinylalcohols, polyesters, and

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copolyesters, can be processed with inorganic filler particles to provide air and moisture breathable films in view of the above description.

In view of the above detailed description, it will be understood that variations will occur in employing the principles of this invention depending upon materials and conditions, as will be understood  
5 to those of ordinary skill in the art.

WHAT IS CLAIMED IS:

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1. An air and moisture breathable biodegradable thermoplastic film comprising

a biodegradable thermoplastic polymer containing a dispersed phase of inorganic filler particles,

5 said film having a liquid impermeable thickness with stretched areas to provide microporosity in the film having a moisture vapor transmission rate MVTR greater than about 1000 g/m<sup>2</sup>/day according to ASTM E96E and air breathability of greater than about 30 cc/cm<sup>2</sup>/min at 90 psi air pressure.

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2. The film of claim 1 wherein the biodegradable thermoplastic polymer is selected from the group consisting of polycaprolactone, starch, polyvinylalcohol, polylactide, polyester, and copolyester, and mixtures thereof.

3. The film of claim 1 wherein said filler is selected from the group consisting of calcium carbonate, silica, talc, barium sulfate, zeolite, and mica, and mixtures thereof.

4. The film of claim 1 laminated to a biodegradable fibrous web.

5. The film of claim 4 wherein the fibers of said fibrous web are selected from the group consisting of a cellulosic polymer, polyester, copolyester, a polymer of entirely L lactic acid, a polymer of entirely D lactic acid, a copolymer of L lactic acid and D lactic acid and a blend of polymers of L lactic acid and D lactic acid.



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6. The film of claim 1 wherein the biodegradable thermoplastic polymer is selected from the group consisting of polyvinyl alcohol (PVA), polycaprolactone (PCL), polylactide (PLA), starch, a blend of starch and PVA, PCL or PLA, polyhydroxy(butyrate) (PHB), polyhydroxy(valerate) (PHV), and aliphatic-aromatic copolyesters, and mixtures thereof.
- 5
7. The film of claim 1 wherein the microporous film has a thickness on the order of about 0.25 to about 10 mils.
8. The film of claim 1 wherein the microporous film has a thickness on the order of about 0.25 to about 2 mils.
9. The film of claim 1 wherein the moisture vapor transmission rate (MVTR) is about 2000 to about 4500 grams per m<sup>2</sup> per day according to ASTM E96E and air permeability is about 200 to about 1600 cc/min/cm<sup>2</sup> at 90 psi air pressure.
10. The film of claim 1 wherein said inorganic filler is selected from the group consisting of calcium carbonate, barium sulfate, mica, talc, silica and zeolite.

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11. A high speed method of making an air and moisture breathable biodegradable thermoplastic film having liquid barrier properties comprising

melt blending about 40% to about 75% by weight of a  
5 biodegradable thermoplastic polymer and about 25% to about 60% by weight of inorganic filler particles to form a biodegradable thermoplastic polymer composition,

extruding a web of said molten thermoplastic composition from a slot die through a cooling zone into a nip of rollers to form a film  
10 having a thickness of about 0.25 to about 10 mils at a speed on the order of at least about 550 fpm to about 1200 fpm without draw resonance,

applying an incremental stretching force to said film at said speeds along the lines substantially and uniformly across said film and  
15 throughout its depth to provide a biodegradable microporous film with an MVTR greater than about 1000 g/m<sup>2</sup>/day according to ASTM E96E, and air breathability greater than about 30 cc/cm<sup>2</sup>/min at 90 psi air pressure.

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12. The method of claim 11 wherein the MVTR is on the order of about 2000 to about 4500 g/m<sup>2</sup>/day according to ASTM E96E and air permeability is about 200 to about 1600 cc/min/cm<sup>2</sup> at 90 psi air pressure.

13. The method of claim 11 comprising introducing a biodegradable nonwoven fibrous web into said nip of rollers and controlling the compressive force to bond the web to the film and stretching to form a laminated biodegradable film.

14. The method of claim 11 wherein the biodegradable thermoplastic polymer is selected from the group consisting of polycaprolactone, starch, polyvinylalcohol, polylactide, polyester, copolyester, and mixtures thereof.

15. The method of claim 11 said filler is selected from the group consisting of calcium carbonate, silica, talc, barium sulfate, zeolite, and mica, and mixtures thereof.

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16. The method of claim 11 wherein the fibers of said fibrous web are selected from the group consisting of a cellulosic polymer, polyester, copolyester, a polymer of entirely L lactic acid, a polymer of entirely D lactic acid, a copolymer of L lactic acid and D lactic acid and  
5 a blend of polymers of L lactic acid and D lactic acid.

17. The method of claim 11 wherein the biodegradable thermoplastic polymer is selected from the group consisting of polyvinyl alcohol (PVA), polycaprolactone (PCL), polylactide (PLA), starch, a blend of starch and PVA, PCL or PLA, polyhydroxy(butyrate) (PHB),  
5 polyhydroxy(valerate) (PHV), and aliphatic-aromatic copolyesters, and mixtures thereof.

18. The method of claim 11 wherein the microporous film has a thickness on the order of about 0.25 to about 10 mils.

19. The method of claim 11 wherein the microporous film has a thickness on the order of about 0.25 to about 2 mils.

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20. The method of claim 11 wherein the moisture vapor transmission rate (MVTR) is on the order of about 2000 to about 4500 grams per m<sup>2</sup> per day according to ASTM E96E.

21. The method of claim 11 wherein said inorganic filler has an average particle size of about 1 to about 10 microns and is selected from the group consisting of calcium carbonate, barium sulfate, silica and zeolite.

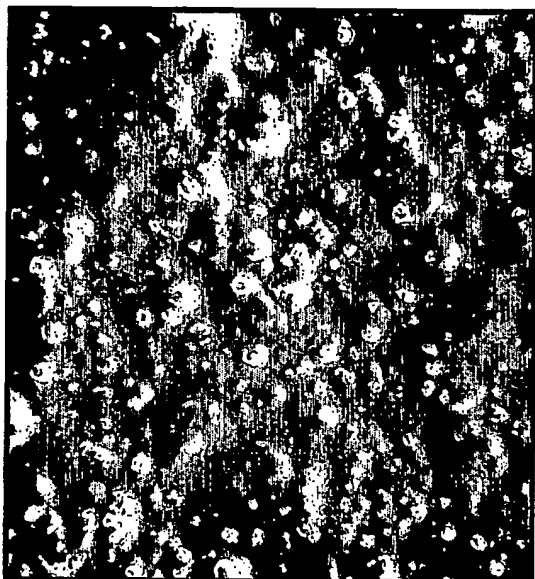


FIG. 1



FIG. 2

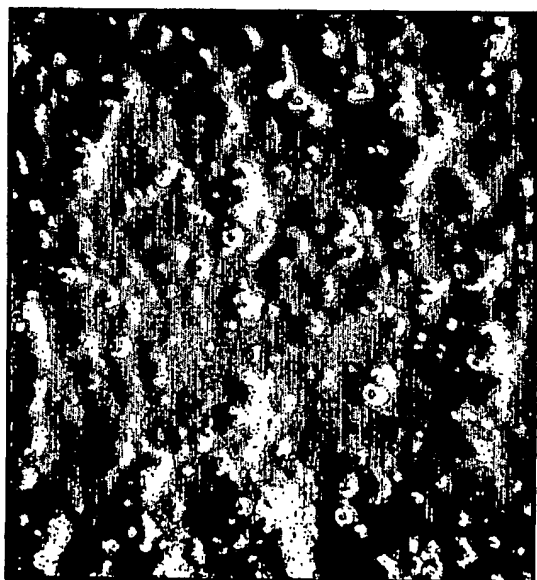


FIG. 3

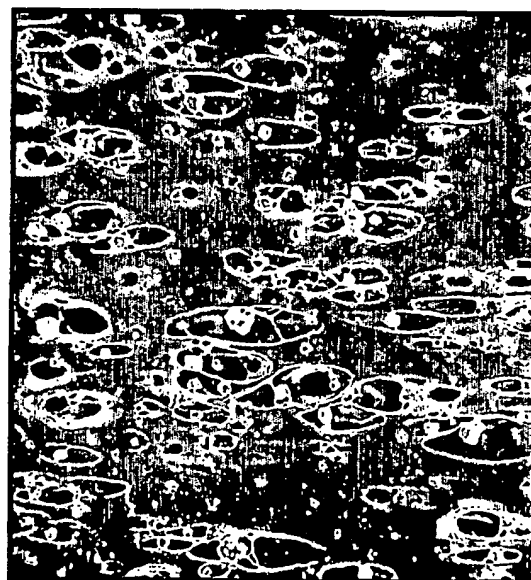


FIG. 4



**FIG. 5**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/20299

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08J5/18 B29C47/88 B32B27/12 B32B31/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08J B29C B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 29909 A (CLOPAY PLASTIC PROD CO) 21 August 1997 (1997-08-21)  claims 1,5,7,8,10,12 page 5, line 14 - line 20 ---	1-8,10, 11, 13-19,21
X	EP 0 510 998 A (MITSUI TOATSU CHEMICALS) 28 October 1992 (1992-10-28) claims 1,5,7 page 5, line 27 - line 28 examples 1-14; table 4 ---	1-3,6-10
P,X	WO 01 19592 A (CLOPAY PLASTIC PROD CO) 22 March 2001 (2001-03-22) claims 1,6-8,14-17,20,25,26,31 page 9, line 19 - line 21 page 14, line 17 - line 21 page 15, line 3 - line 5 ---  -/-	1-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

24 October 2001

Date of mailing of the international search report

08/11/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Niaounakis, M



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/20299

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 03098 A (CLOPAY CORP) 18 February 1993 (1993-02-18) tables 1,4 page 13, line 13 - line 22 table 3 ----	1
A	WO 98 51475 A (PROCTER & GAMBLE) 19 November 1998 (1998-11-19) claims 1,6,9 page 3, line 30 -page 4, line 2 page 6, line 21 - line 27 page 8, line 3 - line 11 ----	1
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 03, 31 March 1997 (1997-03-31) & JP 08 295748 A (DAICEL CHEM IND LTD), 12 November 1996 (1996-11-12) abstract ----	1
A	EP 0 736 563 A (SAFTA SPA) 9 October 1996 (1996-10-09) claims 1,6,8 ----	1
A	US 5 851 937 A (EHRET PHILIPPE ET AL) 22 December 1998 (1998-12-22) cited in the application claim 1 ----	1
E	WO 01 51548 A (CLOPAY PLASTIC PROD CO) 19 July 2001 (2001-07-19) claims 1,4,8-10,21,24-27 page 14, line 20 -page 15, line 1 page 15, line 6 - line 8 page 18, line 22 -page 19, line 3 ----	1-21
A	DATABASE WPI Section Ch, Week 199804 Derwent Publications Ltd., London, GB; Class A23, AN 1998-037109 XP002181001 & JP 09 291163 A (MITSUBISHI CHEM CORP), 11 November 1997 (1997-11-11) abstract -----	1